

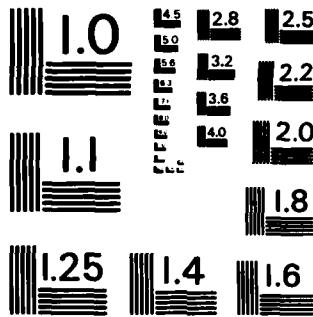
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(20) devices. This program investigates the formation of metal-semiconductor interfaces with some of the most powerful surface-science experimental probes: photoemission spectroscopy with synchrotron radiation, Auger spectroscopy, low-energy electron defraction in high-resolution electron energy loss surface vibrational spectroscopy. The most important results obtained in the period covered by this report are: (1) the study of the influence of interface morphology on the Schottky barrier for the systems GaAs-In and InP-Al; (2) the study of the local stoichiometry at interfaces involving  $Hg_{1-x}Cd_xTe$ ; (3) the study of Al overayers on Si by high resolution electron energy loss; (4) the first study of Schottky barrier formation involving an amorphous semiconductor, Au on a-Si and a-Ge; (5) the development of a new method to obtain AlAs substrates; (6) the study of rare earth overayers on Si and Ge. The stimulated desorption process is potentially a good probe of the chemical properties of adsorbed species, e.g. in catalytic systems. During the period covered by this report we made further progress in improving the signal-to-noise ratio of our original method to detect photon-stimulated desorbed neutral species, and we studied the desorption of solid neopentane.

Annual Report on the Research Program on

PHOTOEMISSION, VIBRATIONAL AND STIMULATED DESORPTION STUDIES  
OF METAL-SEMICONDUCTOR INTERFACES  
AND OF CHEMISORBED ATOMS AND MOLECULES

for the period October 1, 1983 to September 30, 1984

prepared by

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Abstract

This program has produced in recent years a number of fundamental results on the microscopic properties of metal-semiconductor interfaces and on the mechanism of photon stimulated desorption. Both areas of research are of fundamental interest in condensed matter physics. Furthermore, they have important applications in technology. The microscopic metal-semiconductor interface properties are directly related to the behavior and performances of the Schottky barrier, one of the building blocks of modern solid-state devices. This program investigates the formation of metal-semiconductor interfaces with some of the most powerful surface-science experimental probes: photoemission spectroscopy with synchrotron radiation, Auger spectroscopy, low-energy electron diffraction and high-resolution electron energy loss surface vibrational spectroscopy. The most important results obtained in the period covered by this report are: (1) the study of the influence of interface morphology on the Schottky barrier for the systems GaAs-In and InP-Al; (2) the study of the local stoichiometry at interfaces involving  $Hg_{1-x}Cd_xTe$ ; (3) the study of Al overayers on Si by high resolution electron energy loss (4) the first study of Schottky barrier formation involving an amorphous semiconductor, Au on a-Si and a-Ge; (5) the development of a new method to obtain AlAs substrates; (6) the study of rare earth overayers on Si and Ge. The stimulated desorption process is potentially a good probe of the chemical properties of adsorbed species, e.g. in catalytic systems. During the period covered by this report we made further progress in improving the signal-to-noise ratio of our original method to detect photon-stimulated desorbed neutral species, and we studied the desorption of solid neopentane.

## I. INTRODUCTION

This program was supported by the Office of Naval Research for the past three and a half years. The period specifically covered by this report was particularly productive -- 17 articles were published or accepted for publication in refereed journals.<sup>1-17</sup> We shall now give a short description of the most significant results in our different research areas.

## II. METAL-SEMICONDUCTOR INTERFACE MORPHOLOGY

The importance of the interface morphology in the establishment of III-V/metal Schottky barriers was emphasized by the classic theoretical works of Zunger and of other authors.<sup>18</sup> Zunger proposed that the formation of Al islands on GaAs releases the necessary energy to promote the formation of surface defects and stabilize the interface position of the Fermi level as predicted by Spicer's defect model.<sup>19</sup> During the past two years we tested Zunger's hypothesis with different experimental methods, proving its basic validity.<sup>1,20</sup> In particular, we made a novel use of polar-angle-resolved photoemission to probe the Al islands and analyze their composition.<sup>1</sup> The formation of Al islands was also analyzed by studying the GaAs surface core-level shifts during interface formation (see Fig. 1). The changes in the chemical environment of the Al adatoms due to island formation was monitored by core-level photoemission experiments performed on ultrathin Al overlayers.<sup>5,20</sup>

One important byproduct of these investigations was the development of a series of new experimental tools which are now ready to be used for other systems. These are (1) experiments on ultrathin metal overlayers, which we can now routinely perform at the 1/100 monolayer level; (2) analysis of surface core-level shifts, for which we use a VAX computer and a powerful nonlinear least-square program developed by the CERN and adapted to our local VAX; (3) use of polar-angle resolved photoemission to study the interface morphology. We recently extended<sup>7,13</sup> this multiple approach to the study of morphology effects in two other systems, GaAs-In and InP-Al. The GaAs-In results were particularly interesting,<sup>13</sup> since the formation

process of this interface has nothing in common with those of other systems in the same family (we called it the "black sheep in a well-behaved interface family" -- see Fig. 2). First, the final Fermi level pinning position at the interface is not the "canonic" one observed for a wide variety of GaAs interfaces. Second, metal islands are formed at a much earlier stage than for GaAs-Al. Third, these processes are not accompanied by an exchange reaction as in GaAs-Al and InP-Al. We argued<sup>13</sup> that, paradoxically, all these facts strengthen the defect model.<sup>19</sup> We also performed a series of experiments on the morphology of interfaces formed on annealed GaAs surfaces. The corresponding results are being analyzed.

### III. INTERFACES ON NARROW-GAP SEMICONDUCTORS

While the morphology studies require the use of sophisticated techniques, a much simpler approach can yield interesting results on an important but essentially unexplored class of interfaces -- those involving  $Hg_{1-x}Cd_xTe$  and other narrow-gap semiconductors. Synchrotron-radiation photoemission was used to probe the local chemical composition of  $Hg_{1-x}Cd_xTe$  during the interface formation.<sup>2,3,21</sup> We observed in several cases surprisingly large changes induced by chemisorption. For example, during the deposition of Al the local concentration of Hg changes by about a factor of two.<sup>21</sup> These changes have dramatic effects on the local parameters of the narrow-gap semiconductor and therefore on the interface parameters. It is now clear that the interface region has little resemblance with the bulk  $Hg_{1-x}Cd_xTe$ , whose preparation requires a lot of sophisticated - and expensive - chemistry.

The importance of  $Hg_{1-x}Cd_xTe$  for infrared-detecting devices stimulated us to initiate systematic studies of its chemisorption properties.<sup>2,3,21</sup> These studies involved, besides Al, overlayers of Ge, In, Au and H. An example of the corresponding results is shown in Fig. 3. We were able to find a correlation between the reactivity predicted on the basis of bulk chemical parameters and the changes in the local stoichiometry. Due to the complexity of these systems, a more complete systematic work is necessary to

draw general conclusions which can guide the future device research on this material.

Preliminary experiments were performed on other interesting narrow-gap semiconductors and in particular on interfaces involving PbTe.<sup>16,17</sup> These clarified a series of puzzling results concerning the strong degeneracy of the Fermi level in the region near the interface.

#### IV. LOCAL VIBRATIONAL PROPERTIES OF METAL-SEMICONDUCTOR INTERFACES

A general conclusions of our past semiconductor interface studies is that the local chemistry is important in the establishment of the interface parameters, e.g. the Schottky barrier. This stimulated our recent attempts to apply an extremely powerful experimental technique to study interface bonds -- high-resolution electron energy loss spectroscopy.<sup>22</sup> The experiments were performed at the national NSF facility CRISS operated by Montana State University. In preliminary tests we developed the techniques to handle different kinds of ultraclean Si surfaces in the CRISS spectrometer. We were particularly glad to find that cleaved Si surfaces could be routinely studied with a reasonable resolution of 12 - 14 meV. In these experiments we enjoyed collaborating with the competent and friendly personnel of the CRISS facility.

The most recent round of experiments at CRISS was dedicated to a preliminary test of metal-semiconductor vibrational studies. The system under investigation was Al on annealed Si. The results (see for example Fig. 4) are still being processed, but we have an idea of their basic message. We found that the Drude-like tail<sup>22</sup> present in the low-energy spectrum of annealed Si is progressively removed by Al deposition and by the subsequent annealing processes which change the overlayer reconstruction. This tail was attributed to the metallic character of the annealed Si surface. Paradoxically, it would appear that the metallic character of this semiconductor surface is removed by the chemisorption of ... metal atoms! This result is nicely correlated to what we know about the Schottky barrier formation for these systems.<sup>23</sup> It appears that at first the adatoms cause an

unpinning of the Fermi level due to the removal of clean-surface atoms, and only after relatively large coverages they cause a new pinning. This mechanism replaces the old, oversimplified ideas which attributed the interface Fermi-level pinning to clean-surface states.

Another very interesting piece of information is a change in the vibrational frequency induced by high-temperature annealing of Si-Al. This result requires more theoretical input for a reliable interpretation. There is, however, a strong possibility that the change is due to a modification of the adsorption site for Al, not revealed by the previous, extensive experiments performed on these systems.<sup>24</sup> In general, the message from our tests is that surface vibrational spectroscopy can indeed be very helpful in the study of metal-semiconductor interface bonds.

#### V. OTHER CLASSES OF INTERFACES

Some of our recent experiments involved several new classes of interfaces, and in particular preliminary tests of systems which we are planning to study in detail in the next three years. We also completed the study of Al-impurity-enhanced oxidation of Ge with a complete characterization of the oxidation states.<sup>4</sup> This is a short description of the experiments performed on three particularly interesting classes of interfaces.

#### AMORPHOUS SEMICONDUCTOR SUBSTRATES

We are planning to become involved during the next several years in the important and stimulating problem of interface formation on amorphous semiconductors. In preparation for that, we developed the necessary methods to prepare in situ the corresponding substrates. These involve deposition of Ge on Si, electron-bombardment deposition of Si on Ge and ion sputtering of a amorphous and hydrogenated-amorphous samples of Si, Ge, Si-Ge alloys and Si-C alloys provided by the University of Rome. We can now routinely handle all these systems. Preliminary experiments<sup>14</sup> were already performed

on the deposition of Au overlayers on amorphous Si and Ge (see Fig. 5). We found in particular a striking similarity between the local chemical processes involved in the formation of different kinds of Ge-Au interfaces.

#### AlAs SUBSTRATES

These substrates have until now been largely neglected in interface research due to the lack of bulk crystals suitable as substrates. The only approach to solve this problem in the past was a sophisticated in situ use of molecular beam epitaxy. These difficulties are unfortunate since AlAs interfaces are extremely important, e.g. for solid-state lasers in communications.

We recently developed a method to produce in situ good AlAs substrates based on the exchange reaction between GaAs and an Al overlayer. This process was studied in detail, and in particular we found the necessary annealing temperatures to force the exchange reaction and to restore the surface order.

#### RARE EARTH OVERLAYERS

These experiments were performed in collaboration with Alfonso Franciosi and John Weaver (another ONR contractor) of the University of Minnesota. The motivation was the possibility to directly probe with photoemission spectroscopy the rather complex changes in chemical behavior during the interface formation process. This gave us an excellent opportunity to correlate the interface chemistry and the establishment of the interface parameters, an important and somewhat controversial subject.

We studied in particular samarium overlayers on Si and Ge monitoring the interplay between divalent and trivalent configurations.<sup>8,15</sup> We found that the Schottky barrier was established at these interfaces during the very early stage of the interface formation process, with little dependence on the subsequent changes in the local chemistry. This result establishes

for the first time a correlation between the metal-semiconductor interface formation processes for III-V semiconductors and for group IV materials.

## VI. STIMULATED DESORPTION SPECTROSCOPY

Our interest in this area was enhanced by the first detection of neutral species produced by photon stimulated desorption, obtained two years ago.<sup>11,25</sup> One important byproduct of that experiment was the direct evidence that the neutral-to-ion ratio can be extremely large, e.g. larger than  $10^4$ . Therefore, it appeared absolutely necessary not to limit photon stimulated desorption experiments to ions, which are only a small fraction of the entire picture.

The recent months brought several developments in our stimulated desorption studies. We already discussed in our previous report the serious difficulties encountered in extending our detection technique to desorbed neutral hydrogen. The detection is based on the collection of the secondary radiation emitted by the desorbed species as they fly away from the surface, and we were successful in detecting Balmer radiation in the case of hydrogen. However, the signal-to-noise ratio appeared too small for an extensive use of this technique. This stimulated a general search for alternate detection methods resulting in better signal-to-noise ratio. Our efforts are concentrated at present on the use of lasers to artificially pump the desorbed neutral species to an excited states rather than relying on the excitation occurring in some cases during the desorption process.

Preliminary experiments were performed by members of our group at Bell Communication Research in collaboration with Tolk and coworkers to apply this technique to electron stimulated desorption. The results are extremely encouraging. We are now planning to move to Wisconsin a dye laser system provided by our industrial partners to Wisconsin and extend the technique to photon stimulated desorption. Due to the very delicate nature of the instrumentation involved in these tests, we predict that the first results will be available not earlier than one and a half or two years.

We also performed a series of more conventional photon stimulated desorption experiments on ionized species. Particularly interesting appear results recently obtained in collaboration with Jeff Kelber of Sandia about the desorption of solid neopentane (Fig. 6).

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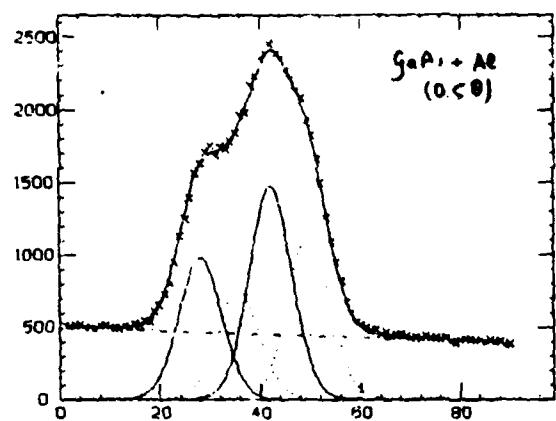
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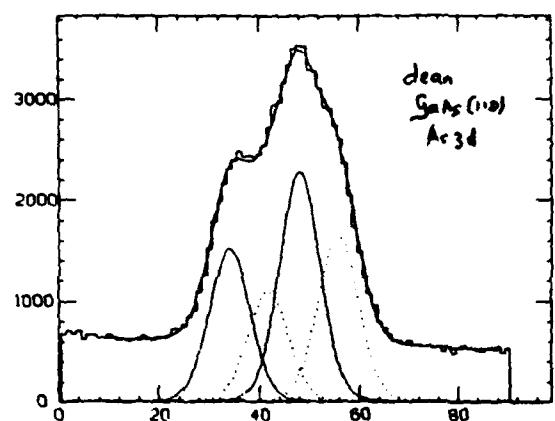


Fig. 1 - Two examples of nonlinear least-square decomposition of the As3d peak showing the surface core-level contributions (dotted lines). The surface core-level shift is the same for clean and Al-covered GaAs. This result is explained by the formation of Al islands.

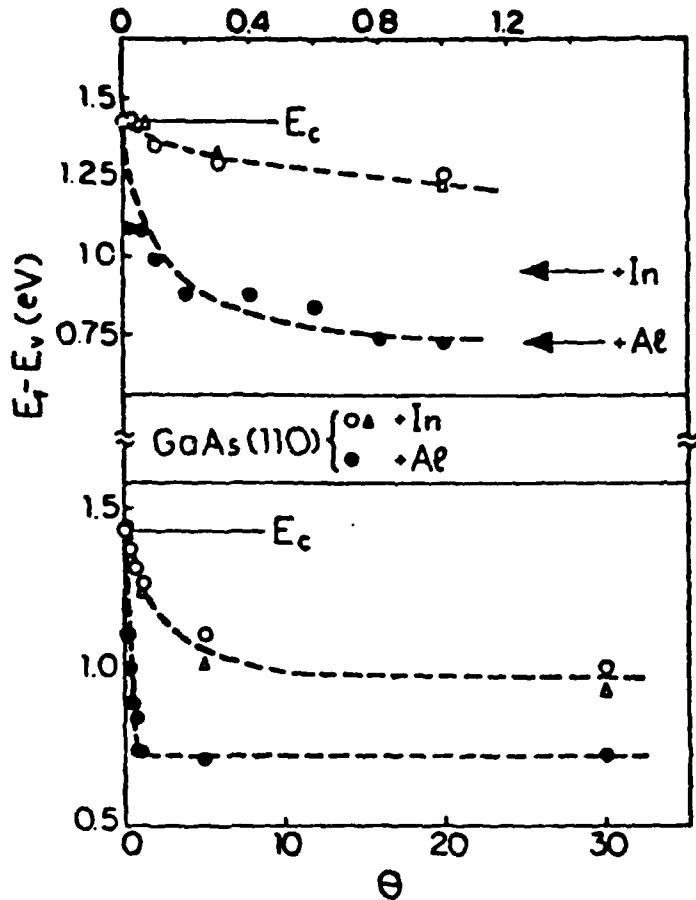


Fig. 2 - The shift of the interface position of the Fermi level emphasizes the anomalous behavior of GaAs-In with respect to other GaAs interfaces, e.g. GaAs-Al (this is the "black sheep" character of GaAs-In discussed in Ref. 13). The shift is much less rapid and saturates to a different position than for GaAs-Al.

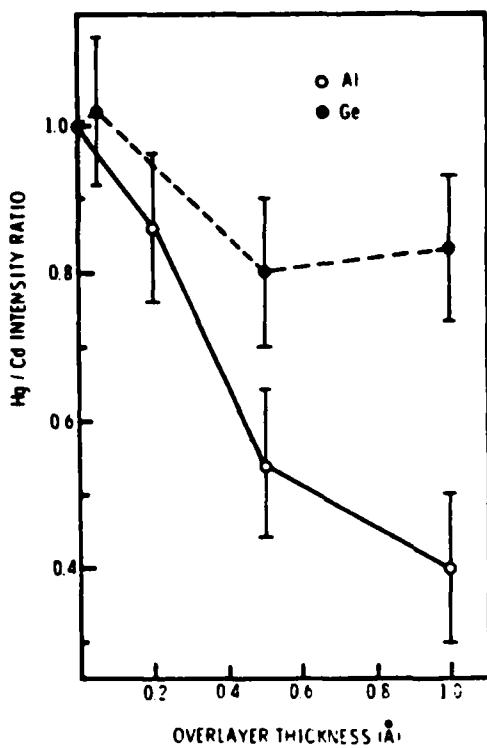
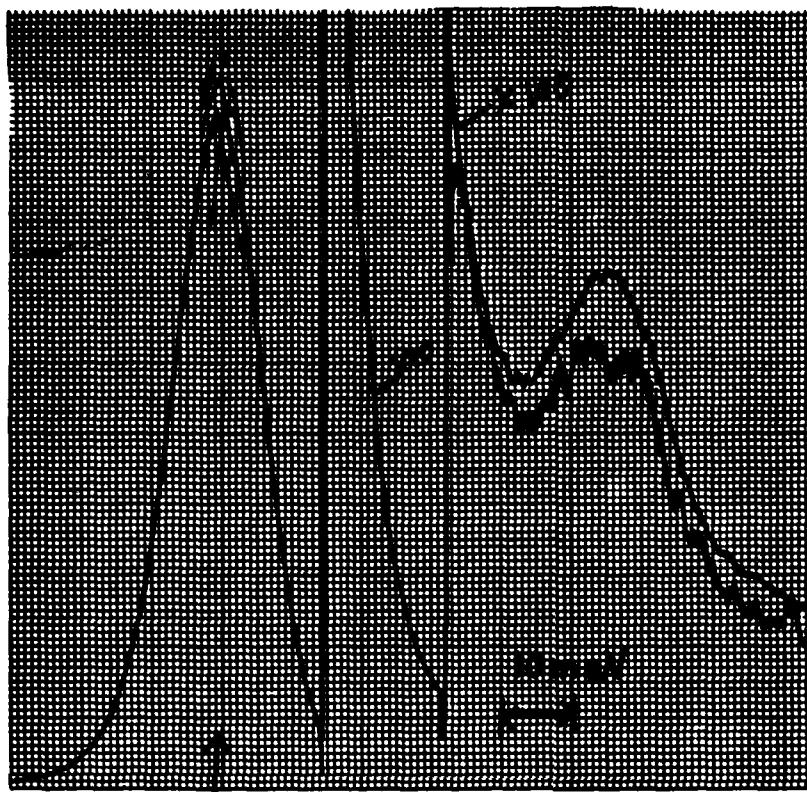


Fig. 3 - The Hg/Cd signal intensity ratio from photoemission spectra taken during the deposition of Al or Ge on  $\text{Hg}_{0.72}\text{Cd}_{0.28}\text{Te}$  (Ref. 3). Notice the dramatic change in the local stoichiometry induced by Al, while the change induced by Ge is much smaller.



Si + Al,  $\theta = 0.5$ , Annealed  
at 700 °C, "7x7" LEED

Fig. 4 - One of the first examples of surface vibrational spectra taken for an Al overlayer on annealed Si(111) with high resolution energy loss spectroscopy. The typical tail of the primary peak has been removed by the Al adatoms, and a characteristic vibrational peak appears at 55 meV. This peak shifts to 65 meV after further annealing at 850°C.

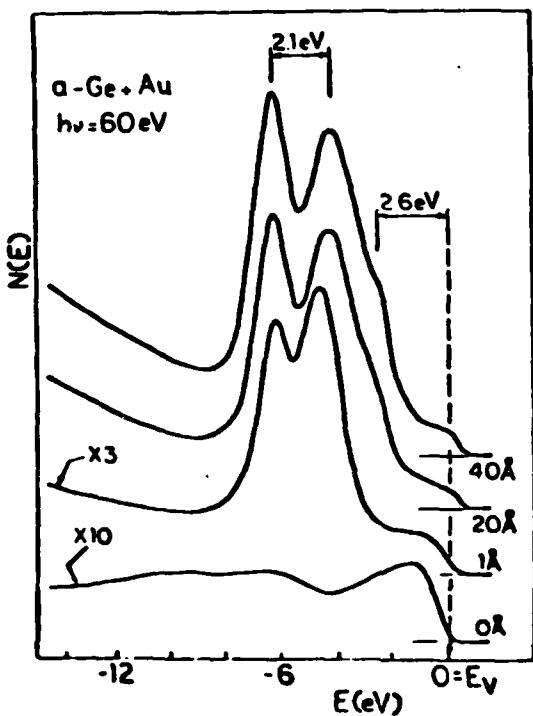


Fig. 5 - Photoemission spectra taken during the Schottky barrier formation on an amorphous semiconductor. The system investigated here is Au on  $\alpha\text{-Ge}$ . The spectra reveal the formation of an interface compound of well-defined stoichiometry (Ref. 23).

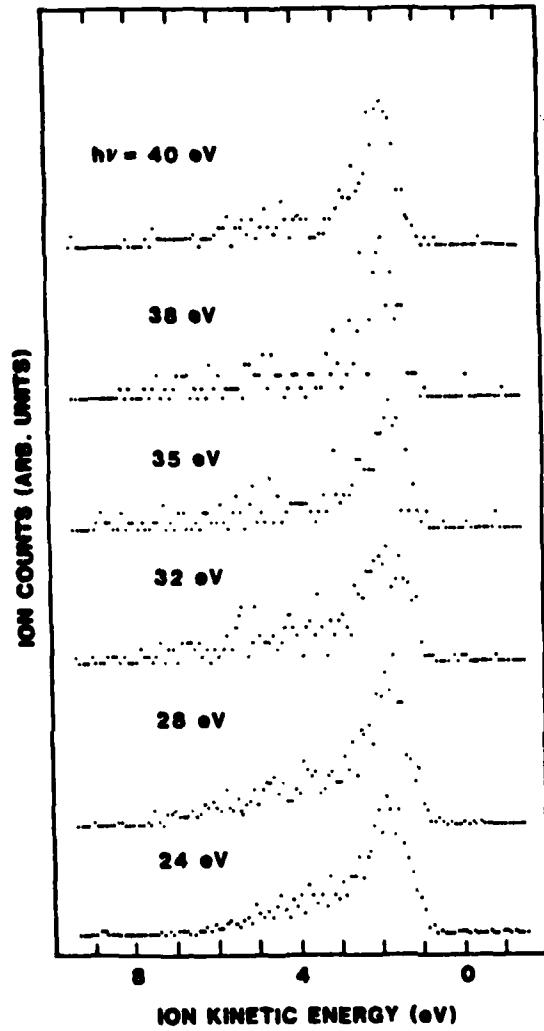


Fig. 6 - An example of experiments on photon stimulated desorption with synchrotron radiation -- ion kinetic energy distribution for different photon energies, obtained from solid neopentane.

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